

A new methodology for the extraction of anharmonic force constants from first principles density functional calculations

K. Esfarjani

*Department of Physics,
Sharif University of Technology, Tehran, Iran,
and Department of Physics, UC Santa Cruz, CA, USA*

Harold T. Stokes

*Department of Physics, Brigham Young University, Salt Lake City, UT, USA
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A new method for extracting force constants (FC) from first principles is introduced. It requires small supercells but very accurate forces. In principle, provided that forces are accurate enough, it can extract harmonic as well as anharmonic FCs up to any neighbor shell. Symmetries of the FCs as well as those of the lattice are used to reduce the number of parameters to be calculated. Results are illustrated for the case of Lennard-Jones potential where forces are exact and FCs can be calculated analytically, and Si in the diamond structure. The latter are compared to previously calculated harmonic FCs.

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I. INTRODUCTION

Two methodologies have been so far developed to calculate force constants (FC) of bulk crystals. One relies on perturbation theory and linear response formalism¹, in which the infinitesimally small displacements of atoms are taken as the perturbing potential, and the required properties, namely the FCs, are calculated as a function of ground state eigenvalues and eigenstates of the crystal by using perturbation theory. The other more traditional method, called the direct method^{2,3,4} requires a small cartesian displacement of an atom placed in a supercell (preferably twice larger than the cutoff range of the FCs). Forces applied to other atoms divided by the small displacement produce the required FCs. This method, however needs also the calculation of Born charges in the case of polar semiconductors, so that FCs due to long-range Coulombic forces can be added analytically to the obtained values. Anharmonic FCs of third or higher order can also be calculated in the same fashion. In the direct method, in principle two small displacements along a given direction are needed in order to fit the produced force with a second order polynomial and extract the harmonic and cubic coefficients. However, we are not aware of any calculation involving three-body (or higher) interactions. Perturbation theory, on the other hand, uses the so-called “2n+1 formula”⁵ to get FCs up to order 2n+1 from a n^{th} order perturbation expansion of the electronic wavefunctions. One can see that the direct method, not being a very systematic one, soon becomes prohibitive if FCs of third or fourth order are needed, given their very large number. The calculation of fourth order, or so-called “quartic” terms becomes also quite involved using the perturbation theory method as now wavefunctions need to be expanded up to second order.

In this paper, we propose a methodology to extract

the harmonic as well as cubic and quartic anharmonic FCs from first-principles calculations in a systematic way. While harmonic FCs are used for the calculation of phonon spectra, vibrational modes and elastic properties, cubic anharmonic FCs give the phonon lifetimes and scattering rates, and quartic ones correct the shift in the phonon frequencies. These quantities are the main ingredients in phonon transport theories which calculate thermal conductivity. They can also be used for constructing a classical molecular dynamics potential of ab-initio accuracy. From such molecular dynamics simulations, thermal conductivity, which can be written as the heat current autocorrelation function⁶ and other thermodynamic properties of bulk or nanostructured materials can be calculated. Phase transformations can also be investigated by using anharmonic potentials.

II. METHODOLOGY

The force constants are defined as derivatives of the potential energy with respect to atomic displacements about their equilibrium position. We write the potential energy in the following form:

$$V = V_0 + \sum_i \Pi_i u_i + \frac{1}{2!} \sum_{ij} \Phi_{ij} u_i u_j + \frac{1}{3!} \sum_{ijk} \Psi_{ijk} u_i u_j u_k + \frac{1}{4!} \sum_{ijkl} \chi_{ijkl} u_i u_j u_k u_l \quad (1)$$

where the roman index i labels the triplet (R, τ, α) with R being a translation vector of the primitive lattice, τ an atom within the primitive unit cell, and α the cartesian coordinate of the atomic displacement u . In other words, u_i is the displacement of the atom (R, τ) in the direction α from its equilibrium or any reference position. Φ, Ψ and

χ are respectively the harmonic, cubic and quartic FCs, whereas Π is the negative of the residual force on atom i , and is zero if the potential energy V is expanded around its minimum or equilibrium configuration. In clusters or molecules the formalism is the same, only the translation vector R needs to be dropped.

The resulting force on atom i would then be:

$$F_i = -\frac{\partial V}{\partial u_i} = -\Pi_i - \sum_j \Phi_{ij} u_j - \frac{1}{2} \sum_{jk} \Psi_{ijk} u_j u_k - \frac{1}{3!} \sum_{jkl} \chi_{ijkl} u_j u_k u_l \quad (2)$$

If one considers a simple FCC Bravais lattice in 3 dimensions, one can discover by inspection that there are 123 harmonic, 4867 cubic and 95663 quartic anharmonic FCs only within the first neighbor shell. Of course they are related by different symmetry properties, which will be used here to reduce their number to respectively to 4, 12 and 56.

A. General symmetries of the problem

The symmetries of the FCs are deduced from rotational and translational invariance of the system, in addition to the symmetries of the crystal itself.

These symmetries are:

-Invariance under the permutation of the indices:

$$\begin{aligned} \Phi_{ij} &= \Phi_{ji} \\ \Psi_{ijk} &= \Psi_{ikj} = \Psi_{jik} = \Psi_{kji} = \dots \\ \chi_{ijkl} &= \chi_{ikjl} = \chi_{ijlk} = \chi_{jilk} = \dots \end{aligned} \quad (3)$$

where i, j, k and l refer to neighboring atoms. This comes about because the force constants are derivatives of the potential energy, and one can change the order of differentiation for such analytic function.

-Invariance under an arbitrary translation of the system:

Translational invariance of the whole system (even if not an ordered crystal) also implies $V(u) = V(u + c)$ and $F(u) = F(u + c)$ (which is easier to use) where $u(t)$ are the dynamical variables, and c is a constant arbitrary shift vector (may be incommensurate with R).

This implies the well-known ‘‘acoustic sum rule’’ (ASR) generalized to higher order FCs:

$$\begin{aligned} 0 &= \sum_{\tau} \Pi_{0\tau}^{\alpha} \quad \forall(\alpha) \Rightarrow \text{Total force on unit cell} = 0 \\ 0 &= \sum_{R_1, \tau_1} \Phi_{0\tau, R_1 \tau_1}^{\alpha\beta} \quad \forall(\alpha\beta, \tau) \\ 0 &= \sum_{R_2, \tau_2} \Psi_{0\tau, R_1 \tau_1, R_2 \tau_2}^{\alpha\beta\gamma} \quad \forall(\alpha\beta\gamma, R_1, \tau_1) \\ 0 &= \sum_{R_3, \tau_3} \chi_{0\tau, R_1 \tau_1, R_2 \tau_2, R_3 \tau_3}^{\alpha\beta\gamma\delta} \quad \forall(\alpha\beta\gamma\delta, R_1 R_2, \tau_1 \tau_2) \end{aligned} \quad (4)$$

so that diagonal terms in these tensors can be defined in terms of their off-diagonal elements, for arbitrary cartesian components. For more details about the proof of these relations and the ones following on rotational invariances, we refer the reader to Ref.⁷.

-Invariance under an arbitrary rotation of the system: Likewise if the system is rotated arbitrarily, the total energy and forces should not change. This leads to the following relations⁷:

$$\begin{aligned} 0 &= \sum_{\tau} \Pi_{0\tau}^{\alpha} \tau^{\beta} \epsilon^{\alpha\beta\nu}, \quad \forall(\nu) \quad (\text{Torque on unit cell} = 0) \\ 0 &= \sum_{R_1, \tau_1} \Phi_{0\tau, R_1 \tau_1}^{\alpha\beta} (R_1 \tau_1)^{\gamma} \epsilon^{\beta\gamma\nu} + \Pi_{0\tau}^{\beta} \epsilon^{\beta\alpha\nu} \quad \forall(\alpha\nu, \tau) \\ 0 &= \sum_{R_2, \tau_2} \Psi_{0\tau, R_1 \tau_1, R_2 \tau_2}^{\alpha\beta\gamma} (R_2 \tau_2)^{\delta} \epsilon^{\gamma\delta\nu} + \Phi_{0\tau, R_1 \tau_1}^{\gamma\beta} \epsilon^{\gamma\alpha\nu} \\ &\quad + \Phi_{0\tau, R_1 \tau_1}^{\alpha\gamma} \epsilon^{\gamma\beta\nu} \quad \forall(\alpha\nu, R_1, \tau \tau_1) \\ 0 &= \sum_{R_3 \tau_3} \chi_{0\tau, R_1 \tau_1, R_2 \tau_2, R_3 \tau_3}^{\alpha\beta\gamma\delta} (R_3 \tau_3)^{\mu} \epsilon^{\delta\mu\nu} \\ &\quad + \Psi_{0\tau, R_1 \tau_1, R_2 \tau_2}^{\delta\beta\gamma} \epsilon^{\delta\alpha\nu} + \Psi_{0\tau, R_1 \tau_1, R_2 \tau_2}^{\alpha\delta\gamma} \epsilon^{\delta\beta\nu} \\ &\quad + \Psi_{0\tau, R_1 \tau_1, R_2 \tau_2}^{\alpha\beta\delta} \epsilon^{\delta\gamma\nu} \quad \forall(\alpha\nu, R_1 R_2, \tau \tau_1 \tau_2) \end{aligned} \quad (5)$$

Here $\epsilon^{\alpha\beta\gamma}$ is the anti-symmetric Levy-Civita symbol, and $(R\tau)^{\alpha}$ refers to the cartesian component α of the reference position vector of the atom τ in unit cell defined by R . Moreover, an implicit summation over repeated cartesian indices is implied.

As we see, rotational invariance relates the second to the third order terms, and the third to the fourth order terms, implying that if the expansion of the potential energy is truncated after the fourth order terms, we need to start with the fourth order terms, and application of rotational invariance rules will give us constraints on third and second order FCs respectively.

B. Point / space group symmetries

The other constraints come from symmetry operations, such as lattice translation, rotation, mirror or any symmetry operation of the space/point group of the crystal/molecule which leaves the latter invariant.

Invariance under a translation of the system by any translation lattice vector R implies the following relations:

$$\begin{aligned} \Pi_{R\tau}^{\alpha} &= \Pi_{0\tau}^{\alpha} \quad \forall(R\tau\alpha) \\ \Phi_{R\tau, R_1 \tau_1}^{\alpha\beta} &= \Phi_{0\tau, R_1 - R\tau_1}^{\alpha\beta} \\ \Psi_{R\tau, R_1 \tau_1, R_2 \tau_2}^{\alpha\beta\gamma} &= \Psi_{0\tau, R_1 - R\tau_1, R_2 - R\tau_2}^{\alpha\beta\gamma} \\ \chi_{R\tau, R_1 \tau_1, R_2 \tau_2, R_3 \tau_3}^{\alpha\beta\gamma\delta} &= \chi_{0\tau, R_1 - R\tau_1, R_2 - R\tau_2, R_3 - R\tau_3}^{\alpha\beta\gamma\delta} \end{aligned} \quad (6)$$

So in an ideal crystal, this reduces the number of force constants considerably (by the number of unit cells, to

be exact), meaning that we will use for the atoms in all the other cells the same FCs as those we have kept for the atoms in the “central” cell.

If a rotation or mirror symmetry operation is denoted by S , we must have:

$$\begin{aligned}\Pi_{S\tau}^{\alpha} &= \sum_{\alpha'} \Pi_{\tau}^{\alpha'} \mathcal{S}_{\alpha,\alpha'} \\ \Phi_{S\tau,S\tau_1}^{\alpha\beta} &= \sum_{\alpha'\beta'} \Phi_{\tau,\tau_1}^{\alpha'\beta'} \mathcal{S}_{\alpha,\alpha'} \mathcal{S}_{\beta,\beta'} \\ \Psi_{S\tau,S\tau_1,S\tau_2}^{\alpha\beta\gamma} &= \sum_{\alpha'\beta'\gamma'} \Psi_{\tau,\tau_1\tau_2}^{\alpha'\beta'\gamma'} \mathcal{S}_{\alpha,\alpha'} \mathcal{S}_{\beta,\beta'} \mathcal{S}_{\gamma,\gamma'} \quad (7) \\ \chi_{S\tau,S\tau_1,S\tau_2,S\tau_3}^{\alpha\beta\gamma\delta} &= \sum_{\alpha'\beta'\gamma'\delta'} \chi_{\tau,\tau_1,\tau_2,\tau_3}^{\alpha'\beta'\gamma'\delta'} \mathcal{S}_{\alpha,\alpha'} \mathcal{S}_{\beta,\beta'} \mathcal{S}_{\gamma,\gamma'} \mathcal{S}_{\delta,\delta'}\end{aligned}$$

where $\mathcal{S}_{\alpha,\alpha'}$ are the 3×3 matrix elements of the symmetry operation S . These symmetry relations impose a **linear** set of constraints on the force constants.

We should note that any physically correct model of force constants must satisfy the invariance relations. On the other hand, we do approximations by truncating the range of FCs and their order in the Taylor expansion of the potential. Therefore imposing the constraints will move their value away from the true value, but has the advantage that they are physically correct, and will for instance reproduce the linear dispersion of acoustic phonons near $k = 0$. So one should keep in mind that an unrealistic truncation to a too short of a range will produce results in disagreement with experiments.

III. IMPLEMENTATION

Given a crystal with its unit cell and atoms, we first identify its symmetry properties and construct the matrices \mathcal{S} . Using the latter, and the equations 3 and 7, independent FCs of each rank are identified. Then a set of force-displacement data calculated from first-principles is constructed. Next, since the data set is (better be) larger than the number of unknown FCs, the linear set of equations 2, 4 and 5 are fitted with this data using a singular value decomposition (SVD) algorithm. In SVD the unknown force constants will be calculated in a least square sense, and furthermore linear dependencies among the equations will not be a problem as the result is projected out of the “zero eigenvalue space”⁸. One has also the option to use the relations 4 and 5 to eliminate some of the FCs in 2 and solve for the remaining FCs. Here one needs to make a judicious choice of FCs to be eliminated. We prefer not to eliminate the FCs and keep the option of checking the violation of the translational and rotational invariances if only relations 2 are used.

The data set can be obtained in several ways: a molecular dynamics run with small initial displacements, randomly moving all atoms by small displacements a few time steps and calculating the forces on all atoms, and finally displacing one atom at a time symmetrically about

its equilibrium position by a small displacement along x,-x,y,-y,z and -z directions and calculating the forces on all other atoms. Experience has shown that the latter works better for the computation of harmonic force constants and two-body force constants in general. For three and four-body FCs one needs to displace at least two and 3 atoms at a time, respectively.

We must add that the data set is obtained not from a unit cell but from displacements performed in a supercell whose size better exceed the range of FCs; otherwise the contribution of images from neighboring supercells might also be included in a considered FC. In some cases, this could lead to errors in the evaluation of FCs. Notice that the exact outcome of this procedure includes, strictly speaking, the contribution of images as well. For instance, in the case of harmonic FCs, instead of $\Phi_{\tau,\tau'}$ actually the sum $\tilde{\Phi}_{\tau,\tau'} = \sum_L \Phi_{\tau,L+\tau'}$, where L is a translation vector of the supercell, will be extracted. Therefore supercells of low symmetry are preferable in order to avoid encountering FCs that can not be determined. For example in a cubic supercell the force constants between the corners of the cube can never be calculated this way since the distance between adjacent corners never changes. It must, furthermore, be emphasized that the size of the data set as well as its accuracy are crucial in determining the correct set of force constants.

IV. RESULTS

To check the feasibility and accuracy of the method, we first used the Lennard-Jones (LJ) pair force, for which derivatives can be analytically calculated and compared to our results. Furthermore, the LJ forces are accurate within the printed number of digits by the computer, and do not suffer from any convergence or roundoff error problems. First we considered an FCC-Bravais crystal of LJ particles with integer cartesian coordinates. Particles were confined to interact only with their first neighbor. It was found that choosing a very small set of displacements (of the order of 0.001) produced the best results. Since in both the MD data and the fitting procedure the cutoff was set so that only first neighbors interact, the SVD procedure reproduced the exact FCs remarkably well: the error in the harmonic, cubic and quartic FCs was in the 7th, 5th and 4th digits respectively.

As a more stringent test, and in order to get confidence on the accuracy of the fitting method for a real material such as Si, we also considered a diamond structure of LJ particles with interactions up to 10th nearest neighbor, but limited them in our fitting up to the 8th neighbor only. The energy unit was taken to be one and the length unit σ was taken to be equal to the first neighbor distance ($\sqrt{3}/4$). No MD was performed, instead we only displaced the first atom by 0.0005 and 0.001 along the x direction and recorded the forces on all other atoms in a $3 \times 3 \times 3$ cubic supercell of 216 atoms. The results are summarized in table I. Three-body forces are found to

be respectively 5 and 3 orders of magnitude smaller than the largest two-body values in cubic and quartic FCs. It is worth noticing that the fitted values obtained imposing the invariance relations are slightly worse than when invariances are not imposed. This is because some of the longer range FCs (9th and 10th neighbors) were neglected in the fitting procedure, and as a result the values of the included FCs are slightly affected when invariance relations are imposed. In a real material case however, it is more important to have physically correct FCs, even though their values might not be exact. In any case, this can be checked by comparing the results with and without imposing invariance constraints. Imposing the constraints conditions in the SVD procedure results in the violation of the latter by typically 10^{-8} , whereas the force-displacement data could be violated giving relative errors as large as a few percent, if the chosen cutoff is too short or first-principles forces are not very accurate, or displacements are too large.

The same procedure was followed to extract FCs for a real material case: Silicon (diamond). In this case, the range of FCs is unknown and probably longer-ranged than we can exactly handle. The range of harmonic FCs was limited to 8 neighbors, that of the cubic coefficients was limited to 2, and quartic FCs were limited to nearest-neighbor interactions. First we used a data set, similar to the previous LJ calculation, where atoms were displaced by 0.008 and 0.016 Å along all 3 directions in order to minimize systematic and round-off errors which occur in first-principles calculations. LDA-based ultra-soft pseudopotentials were used within the VASP density functional simulation package⁹. A cutoff energy of 300 eV and a single K-point (1/4,1/4,1/4) was used in the $3 \times 3 \times 3$ cubic supercell of 216 atoms.

This was the largest system we could handle. Perhaps more accurate determination of forces using more K-points and a higher cutoff energy would give better results.

In table II harmonic FCs are compared to a recent calculation¹⁰ based on density-functional perturbation theory^{1,5}.

The phonon spectrum obtained by including harmonic force constants up to 8th neighbors is plotted in Fig. 1 versus experimental data points.

V. DISCUSSIONS

The test example of Lennard-Jones potential shows that provided the actual calculation of force-displacements is extremely accurate, it is possible to extract harmonic, cubic and quartic force constants with relatively good precision, by using the above method. Choosing low-symmetry supercells may be advantageous and avoids heavy calculations in big supercells. Our experience on Si has shown that it is possible to extract FCs of Silicon up to the fifth neighbor by using a small 12 atom ($1 \times 2 \times 3$) supercell. But longer-range FCs

| FCs | Nb-Shell | Exact | SVD |
|-----------------------------|--|-------------|---------------------|
| $\Phi_{1,1}^{xx}$ | 0 (0,0,0) | 711.01623 | 711.016 |
| $\Phi_{1,2}^{xx}$ | 1 ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) | -181.33329 | -181.333 |
| $\Phi_{1,2}^{xy}$ | | -213.33328 | -213.333 |
| $\Phi_{1,1}^{xx}$ | 2 ($\frac{1}{2}, \frac{1}{2}, 0$) | 1.497986 | 1.49799 |
| $\Phi_{1,1}^{yy}$ | | -0.5660705 | -0.56607 |
| $\Phi_{1,1}^{xy}$ | | 2.064056 | 2.06406 |
| $\Phi_{1,1}^{xz}$ | | 0 | 2×10^{-15} |
| $\Phi_{1,2}^{xx}$ | 3 ($-\frac{1}{4}, -\frac{1}{4}, -\frac{3}{4}$) | -0.0502417 | -0.050242 |
| $\Phi_{1,2}^{zz}$ | | 0.9066605 | 0.906668 |
| $\Phi_{1,2}^{xy}$ | | 0.1196113 | 0.119612 |
| $\Phi_{1,2}^{xz}$ | | 0.3588383 | 0.358840 |
| $\Phi_{1,1}^{xx}$ | | 0.2700770 | 0.270080 |
| $\Phi_{1,1}^{zz}$ | 4 (1,0,0) | -0.0390294 | -0.039029 |
| $\Phi_{1,2}^{xx}$ | | 0.05459899 | 0.0545990 |
| $\Phi_{1,2}^{zz}$ | 5 ($-\frac{3}{4}, -\frac{3}{4}, -\frac{1}{4}$) | -0.0114737 | -0.0114737 |
| $\Phi_{1,2}^{xy}$ | | 0.07433175 | 0.0743320 |
| $\Phi_{1,2}^{xz}$ | | 0.02477725 | 0.0247773 |
| $\Phi_{1,1}^{xx}$ | | 0.0025635 | 0.0025635 |
| $\Phi_{1,1}^{zz}$ | 6 ($\frac{1}{2}, \frac{1}{2}, 1$) | 0.0335998 | 0.0336000 |
| $\Phi_{1,1}^{xy}$ | | 0.0103455 | 0.0103454 |
| $\Phi_{1,1}^{xz}$ | 6 | 0.0206909 | 0.0206909 |
| $\Phi_{1,1}^{yz}$ | | 0.0206909 | 0.0206909 |
| $\Phi_{1,2}^{xx}$ | 7 ($\frac{1}{4}, \frac{1}{4}, \frac{5}{4}$) | -0.00342573 | -0.0034258 |
| $\Phi_{1,2}^{zz}$ | | 0.03109080 | 0.0310910 |
| $\Phi_{1,2}^{xy}$ | | 0.00143819 | 0.0014382 |
| $\Phi_{1,2}^{xz}$ | | 0.00719095 | 0.0071910 |
| $\Phi_{1,2}^{xx}$ | 7 ($-\frac{3}{4}, -\frac{3}{4}, -\frac{3}{4}$) | 0.00807978 | 0.0080798 |
| $\Phi_{1,2}^{xy}$ | | 0.01294370 | 0.0129437 |
| $\Phi_{1,1}^{xx}$ | 8 (1,1,0) | 0.00739133 | 0.0073913 |
| $\Phi_{1,1}^{zz}$ | | -0.00246785 | -0.0024678 |
| $\Phi_{1,1}^{xy}$ | | 0.00985918 | 0.0098592 |
| $\Phi_{1,1}^{xz}$ | | 0 | 2×10^{-13} |
| $\Psi_{01,01,02}^{xxx}$ | | 2673.7772 | 2673.793 |
| $\Psi_{01,01,02}^{xxy}$ | | 4380.4434 | 4380.590 |
| $\Psi_{01,01,02}^{xyx}$ | | 5233.7765 | 5234.127 |
| $\Psi_{01,01,11}^{xyx}$ | | 4.128112 | 4.1267 |
| $\Psi_{01,01,11}^{yyy}$ | | -5.453064 | -5.4645 |
| $\Psi_{01,01,11}^{yzy}$ | | -13.70929 | -13.705 |
| $\chi_{01,01,02,02}^{xxxx}$ | | -19342.219 | -19401.9 |
| $\chi_{01,01,02,02}^{xyxy}$ | | -96255.978 | -96202.6 |
| $\chi_{01,01,02,02}^{xxxy}$ | | -71907.540 | -71896.1 |
| $\chi_{01,01,02,02}^{xyxz}$ | | -113777.75 | -113727.9 |

TABLE I: Comparison between analytical and numerically extracted (SVD) values of the LJ force constants in the diamond structure, when invariance relations 4 and 5 were not imposed, and only 8 neighbor shells were included in the fitting. Real interactions were included up to 10 neighbors ($R_{\text{cut}} = 1.6$). Subscripts in the first column refer to first or the second atom in the primitive cell (τ index for Φ and $R\tau$ index for Ψ and χ), while superscripts refer to the cartesian coordinates (α index).

would require larger cells because the fitting would fail in this case. In fact, large supercells are really needed for the extraction of longer-range harmonic FCs. Once the latter are known, it is possible to freeze them and extract higher-order FCs from a smaller size supercell but more accurate calculation. In this case, the force-displacement

| FCs | Nb-Shell | Aouissi et al. ¹⁰ | SVD |
|-------------------|--|------------------------------|---------|
| $\Phi_{1,1}^{xx}$ | 0 (0,0,0) | 13.445 | 13.264 |
| $\Phi_{1,2}^{xx}$ | 1 ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) | -3.2796 | -3.2269 |
| $\Phi_{1,2}^{xy}$ | 1 | -2.2875 | -2.2540 |
| $\Phi_{1,1}^{yy}$ | 2 ($\frac{1}{2}, \frac{1}{2}, 0$) | -0.1827 | -0.1873 |
| $\Phi_{1,1}^{yz}$ | 2 | -0.1768 | -0.1788 |
| $\Phi_{1,1}^{xz}$ | 2 | 0.1078 | 0.1070 |
| $\Phi_{1,1}^{zz}$ | 2 | 0.4177 | 0.4065 |
| $\Phi_{1,2}^{xx}$ | 3 ($-\frac{1}{4}, -\frac{1}{4}, -\frac{3}{4}$) | 0.0321 | 0.0324 |
| $\Phi_{1,2}^{xy}$ | 3 | -0.0340 | -0.0354 |
| $\Phi_{1,2}^{yz}$ | 3 | 0.0272 | 0.0283 |
| $\Phi_{1,2}^{zz}$ | 3 | 0.0068 | 0.0073 |
| $\Phi_{1,1}^{xx}$ | 4 (1,0,0) | -0.019 | -0.0239 |
| $\Phi_{1,1}^{zz}$ | 4 | -0.0058 | -0.0072 |
| $\Phi_{1,2}^{xx}$ | 5 ($\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$) | -0.0175 | -0.0197 |
| $\Phi_{1,2}^{xy}$ | 5 | -0.0272 | -0.0265 |
| $\Phi_{1,2}^{yz}$ | 5 | 0.0554 | 0.0573 |
| $\Phi_{1,2}^{zz}$ | 5 | -0.175 | -0.175 |

TABLE II: Comparison between harmonic force constants of Si. Again invariance relations 4 and 5 were not imposed in the fitting, but were included by correcting $\Phi_{11}^{\alpha\beta}$. Up to 8 neighbor shells were included in the fitting. For brevity, we report the results on the first 5 shells. Units are in $eV/\text{\AA}^2$

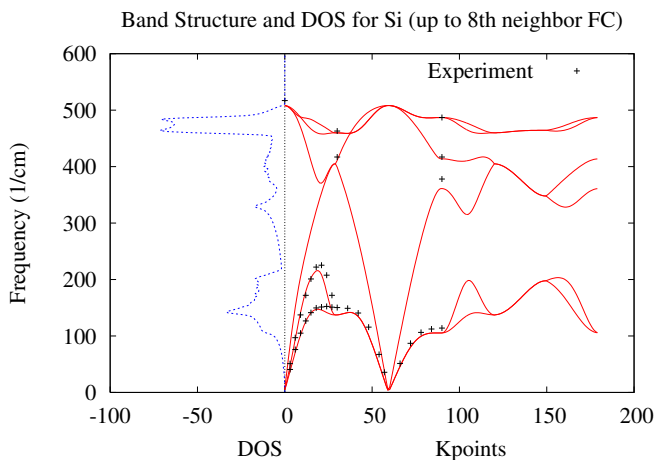


FIG. 1: Phonon band structure of Si using up to 8th neighbor FC.

data can come from a molecular dynamics run of small amplitude, as more than one particle is needed to move in order to extract three and four-body terms.

In case the so-developed potential is going to be used for performing large-scale molecular dynamics (MD) simulations, one does not even need to include harmonic

(and anharmonic) FCs beyond a few, say 4 or 5, neighbor shells. In fact most classical force fields have shorter range. Although MD runs might be more time-consuming with this method, it has the advantage of higher accuracy. Lattice distortions and defects can also be treated using this potential, as the new force constants of the new atomic configuration can be obtained from the already developed Taylor expansion:

$$\begin{aligned}
 \Phi_{new} &= \Phi + u_0\Psi + u_0u_0\chi/2 \\
 \Psi_{new} &= \Psi + u_0\chi \\
 \chi_{new} &= \chi
 \end{aligned}
 \tag{8}$$

in which the static displacement u_0 is due to external forces, and would be obtained by solving $F(u_0) = 0$ where the force F is calculated from Eq. 2.

An additional complication arises when one is dealing with polar or ionic materials. In such cases Born effective charges need to be calculated and their long-range effect on the FCs calculated separately using the Ewald summation or multipole expansion methods. Care must be taken since its short-range part is already included in the extracted FCs. So it needs to be properly subtracted from the Ewald sum contribution. Needless to say, this problem is present in all polar materials, and can not be bypassed.

Using the extracted cubic force constants, one can calculate phonon lifetimes and frequency shifts. Details of such calculations will be published elsewhere.

VI. CONCLUSIONS

To summarize, we have developed a method to extract harmonic, cubic and quartic force constants of any crystal from first-principles force-displacement data. The methodology uses symmetries of the crystal to reduce the number of independent FCs, and can include up to any number of neighbor shells in principle. It requires, however very accurate first-principles data, in order to produce reliable FCs. This method paves the way for the development of a new generation of interatomic potentials of ab-initio accuracy.

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